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CONCENTRATION AND DISTRIBUTION OF COPPER, ZINC AND CADMIUM IN CONTAMINATED SOILS NEAR THE METALLURGICAL PLANT OF ELBASAN IN ALBANIA

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Introduction

Heavy metal contamination in the soil-water-plant ecological system is of great concern because of possible influence on the food chain. In order to evaluate the natural concentration variations of heavy metals and to assess heavy metal contamination in soils, it is necessary to survey trace metal background levels. This is important to be able to understand their biogeochemical behaviours, and to examine their migration and distribution during pedogenesis process.

In the last decade, human activity has continuously increased the levels of heavy metals circulating in the environment. Because sedimentation of particulate material is one of the most important fluxes in the aquatic system, a knowledge of trace metal concentration in sediment and soils can play a key role in detecting sources, evaluating the degree of pollution, and distribution mechanisms, especially in protected areas.

The World Bank has declared that the area located around the metallurgical complex of Elbasan is one of Albania's most important “hot spots”. This is the biggest metallurgical complex in Albania established in the central part of the country. It was built by the Chinese in 1976 and is currently operated by a Turkish firm. It has a treatment capacity of 800 thousand tons/year of iron-nickel ores.

This metallurgical operation, although still using the original technology installed in 1976, plays a major role in the industrial base of the Elbasan area, although the metallurgical activity has always been an environmental hazard. According to the World Bank, this metallurgical plant released in 1991 an estimated 44.8 tons of toxic dust/year. The contaminants emitted from this complex have, perhaps, the most effect on the Shkumbini River, the main watershed for the region.

Smelters, whose emissions contain toxic gases and dusts rich in heavy metals like Pb, Cu, Zn Cr, Ni and Cd, caused particularly dangerous effects. Therefore, the Shkumbini is among the more polluted rivers in Albania. Nevertheless, its waters are used to irrigate agricultural crops downstream.

The pollution emitted from this complex has caused many problems to the microenvironment and has had adverse effects on the health of various categories of peoples, especially pregnant and lactating mothers. Problems of professional diseases are very evident in this area. They have been caused by the presence of toxic gases, vapours, and dust. The World Bank observed in 1993 that flora modifications are generally present on soils contaminated by industrial and mines discharges. Consequently, its impact on the agroenvironment cannot be dismissed, not least in Albania where laws preventing such discharges, if extents at all, are not enforced.

According to statistical data, the Elbasan district is one of the major agricultural areas of the country, providing produce both for the Elbasan area and the capital city of Tirana. The region is endowed with good soils and climate. However, because of the industrial activity of the metallurgical complex, the soils around it are very contaminated by heavy metals such as cadmium, nickel, chromium, lead, and copper.

Vegetables and other crops grown in this area present a serious health risk for consumers. These soils are, therefore, very contaminated and require attention. The adverse effects on the human population include the following: (i) loss of high quality farmland and pollution of soil and groundwater, (ii) enhanced demand for clean water, contamination of urban areas and increased public health problems, and (iii) low grazing quality and reduced crop yields and livestock production.

Based on those considerations, an immediate action is required to ameliorate the situation, since the natural resources (soil, water, and air) have been contaminated. Sustainable development of this area would increase the income of the associated communities, increase their property values, and improve the health situation.

Recent studies by several investigators have shown that atmospheric fallout from ore smelters can contribute significantly to soil contamination with heavy metals (Goodman and Roberts 1972, Cartwright *et al.,* 1977, Franzin *et al.,* 1979, Kuo *et al.,* 1983). Metal deposition patterns, though depending to a considerable extent on climatic conditions (i.e. wind and rainfall distribution), (Cartwright *et al.,* 1977; Franzin *et al.,* 1979), generally decline exponentially with distance from the smelter.

Consequently, metal concentrations in soils near the smelter may be elevated significantly and may pose a significant health hazard. The total soil metals concentration can be used to estimate the degree of soil exposure to heavy metal contamination, but they are not generally well correlated with plant uptake of metals (Baker and Chesnin 1975).

Such metals as Cu and Zn may exist in soils or sediments in various fractions (exchangeable, carbonate-bound, oxide-bound, organic matter-bound, or incorporated in crystal lattices) (McLaren and Crawford 1973, Gibbs 1977, Tessier *et al.,* 1979). The distribution of metals with various forms depends on the existing chemical and mineral environment. The dominant forms of the metals that are present will control the relative impact of elevated metals on soil-plant systems.

Availability to plants may be governed in turn by dynamic equilibrium involving these metal fractions, rather than by total metal contents *per se* (Elsokkary and Lag 1978). Investigation of various metal fractions in contaminated soils should be of importance for estimating the amounts of metals potentially available to plants within relatively short span of time.

The objectives of this study were to: (i) determine the degree of soil contamination by Cu, Zn, and Cd, with respect to distance from the metallurgical complex of Elbasan, Albania, and (ii) determine various metal fractions for selected soil samples. The data gathered from this study will allow the evaluation of soil-management techniques to limit mobility and plant availability of heavy metals and to ultimately minimise their transfer into the food chain.

Materials and Methods

Sampling site

The Metallurgical plant is located in Elbasan, in the centre of Albania, near the Shkumbini river, about 60-km south-east from Tirana. The population of the are accounts for about 120,000 inhabitants. The metallurgical complex is located in the south-western part of the Elbasan city roughly 2-3 km far from the city.

The climate is Mediterranean type with hot and dry summers and mild and wet winters. The average rainfall is about 1,300 mm per year, however the majority of rains happen during the fall and winter season. The temperature varies from as low as 3 in the winter to 35^0C during the summer time.

Soil sampling, preparation, and analyses

In 1998, approximately 80 surface soil samples (0-20 cm) were collected from the different locations according to the distance from the metallurgical plant. The distance of these sites from plant was approximately 1, 2, 3, 4, 5, 6 and 7 km. Sub samples of each soil were air-dried and ground to pass through a 2-mm stainless-steel sieve. The main characteristics of these soils are given in Table 2.

Soil pH was determined in 1:2.5 soil to $CaCl_{2,}$ CEC by Mehlich method, organic C by elementary analysis, $CaCO_3$ by the Scheibler method and particle-size distribution by the combination of pipette and sieving method. Total content of heavy metals were determined by the mineralisation of soil samples in the solution of aqua regia (HCl and HNO_3) in the ratio 3:1).

Fractionation procedure

A sequential fractionation procedure was used to partition Cu, Zn and Cd into exchangeable (EX), carbonates (CARB), organic matter (OM), Mn oxide (MnOX), amorphous Fe oxide (AFeOX), crystalline Fe oxide (CFeOX), and residual (RES) fractions.

Reagents used in the fractionation scheme were selected from those cited in the literature as being selective for the specific chemical form in soils and all analyses are carried out near the Institute of Soil Science & Conservation, Gieesen Germany. The sequential extraction procedure is given in Table 1.

Table 1 Sequential extraction procedure for Copper, Zinc and Cadmium in soil.

Fraction	Solution	g soil/ml solution.	Conditions	Reference
1. Exchangeable (EX)	1 M $Mg(NO_3)_2$	10:40	Shake 2 h	(Tessier et al. 1979)
2. Carbonates (CARB)	1 M NaOAC (pH5.0, CH_3COOH)	10:40	Shake 5 h	
Organic Matter (OM)	0.7 M NaOCl (pH 8.5)	10:20	30min in boiling water bath. Stir occasionally. Repeat extraction	(Shuman 1983)
4. Mn oxides (MnOX)	0.1 M NH_2OH. HCl (pH2, HNO_3	5:50	Shake 30min	(Chao 1972)
5. Amorphous Fe oxides (AFeOX)	0.25 M NH_2OH.HCl + 0.25 M HCl	5:50	Shake 30 min at 50oC in water bath	(Chao and Zhou 1983)
6. Crystalline Fe oxides (CFeOX)	0.2 M $(NH_4)_2$ C_2O_4 + 0.2 M $H_2C_2O_4$ (pH3) + 0.1 M ascorbic acid	5:50	30 min in boiling water bath. Stir occasionally	(Shuman 1982)
7. Residual (RES)	Conc. HF, Con. $HClO_4$ and conc. HCl in sequence			(Tessier et al. 1979)

Results and Discussions

Figures 1a, 1b and 1c show the distribution of total Cu, Zn and Cd in soil samples (0-20 cm) with respect to distance from the metallurgical plant of Elbasan. Total metal concentrations of the soil samples (Figure 1a, 1b, and 1c) show a wide range of values, from background to a level considered to reflect gross contamination.

For Cu the range is from 50 to 159 mg/kg soil, Zn 86 to 147 mg/kg soil and Cd 0.76 to 2.25-mg/kg soil. An intense reduction in concentrations of these metals with distance was observed. Our data shows high levels of heavy metal content within the 2 to 5 km distances from the Metallurgical complex. The same results are observed and from other authors in their studies about heavy metal concentration near this metallurgical plant (Shallari, *et al,* 1998).

Table 2: Physical and chemical characteristics of soil samples used

Soil number	PH (1:2)	CEC Cmol(+)kg^{-1}	Organic matter gkg^{-1}	$CaCO_3$ gkg^{-1}	Sand gkg^{-1}	Silt gkg^{-1}	Clay gkg^{-1}
1	7.8	7.65	6.2	12.6	715	113	172
2	7.6	3.26	5	13.5	836	85	79
3	8.1	6.95	5.5	15.2	665	119	216
4	7.6	8.56	4	21.8	773	117	110
5	7.5	7.98	9.6	22.3	653	259	88
6	6.8	15.6	10.2	25.5	546	245	209
7	7.7	23.5	11.6	16.3	652	185	163
8	7.9	7.85	12.3	25.9	506	215	279
9	7.1	5.63	12	27.5	658	231	111
10	7.2	10.2	4.5	26.5	674	238	88
11	7.6	11.3	3	26.2	705	194	101
12	7.7	12.3	5	23.5	745	162	93
13	7.3	9.5	2	25.5	716	156	128
14	7.9	6.5	5	12.3	745	146	109

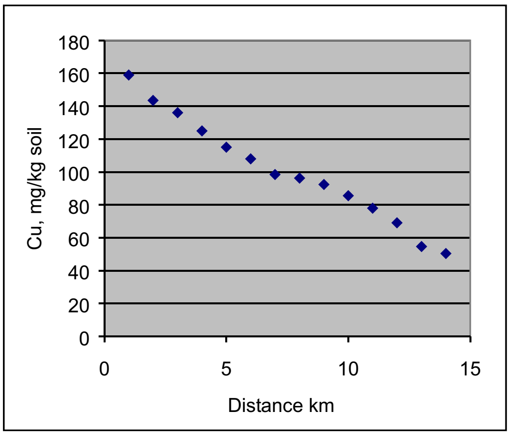

Figure 1a

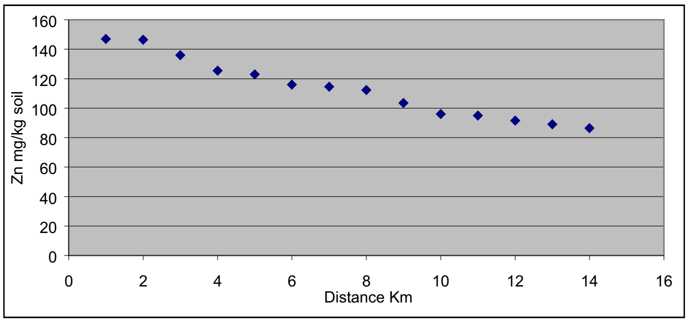

Figure 1b

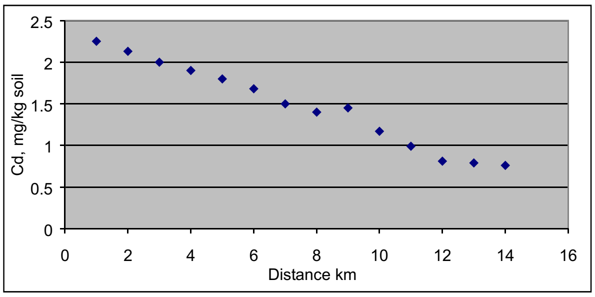

Figure 1c

Figure 1. Distribution of total Cu, Zn and Cd in relation to distance from the Metallurgical plant of Elbasan. (1a) Cu, (1b) Zn, (1c) Cd.

The fractionation data presented in Tables 3, 4 and 5 are averages of metal concentrations in each fraction, expressed in mg kg[1] for each fraction. These data show the various fractions of Cd, Zn and Cu for the soil samples examined.

Table 2. Distribution of Cu in different fractions for 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg^{-1})

Soil number	EX	CARB	OM	MnOX	AFeOX	CFeOX	RES	Sum	Total
1	4.3	3.5	1.5	1.2	18.8	26.2	101.7	157.9	159
2	4.9	4.5	1.6	1.35	19.6	25.5	85.3	142.8	143.5
3	4.1	7.8	1.45	ND	17.3	25.3	79.6	135.6	136
4	5.2	6.3	1.3	1.18	18.2	27.1	65.2	124.5	125
5	3.3	5.2	1.5	1.26	16.2	23.3	62.2	113	115
6	3.5	9.6	1.4	ND	15.2	22.3	53.5	105.5	108
7	3.4	3.2	1.3	ND	13.9	20.5	53.7	96	98.5
8	2.3	5.2	1.2	ND	12.4	17.6	53.8	92.5	96.3
9	2.1	2.3	1.5	1.2	12.9	17.5	53	90.5	92.4
10	2.9	6.3	1.4	1.2	11.8	16.8	49.9	84.3	85.5
11	2.9	3.2	1.5	1.15	8.9	13.5	46.3	77.5	78
12	2.8	2.9	1.4	1.18	5.6	11.8	39.3	65	69
13	2.8	2.6	1.4	1.3	5.2	11.6	27.1	52	54.6
14	2.5	2.5	1.3	ND	4.8	10.2	26.9	48.2	50.4
Mean	3.3	4.6	1.3	1.1	12.2	19.2	56.9	98.6	101

Table 3. Distribution of Zn in different fractions for the 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg^{-1})

Soil number	EX	CARB	OM	MnOX	AFeOX	CFeOX	RES	Sum	Total
1	2.6	3.5	1.9	3.8	5.2	6.8	121.9	145.7	146.5
2	2.5	3.4	1.9	3.7	5.6	7.1	120.6	144.8	147
3	2.4	3.3	1.8	3.6	5.4	7.3	110.9	134.7	136
4	2.2	3.1	1.6	3.5	5.1	6.2	102.1	123.8	125.5
5	2.3	3.0	1.5	3.4	5.2	6.8	99	121.2	123
6	2.1	3.1	1.7	3.6	5.1	6.4	92.8	114.8	116
7	2.2	3.0	1.8	3.7	5.3	6.1	91.8	113.9	114.5
8	2.1	2.9	1.6	3.5	5.2	5.8	89.3	110.4	112.3
9	2.0	3.3	1.8	3.2	4.4	5.6	81.4	101.7	103.5
10	2.1	3.6	1.9	3.4	5.2	5.3	73.3	94.8	96
11	2.0	3.5	1.8	3.2	6.2	6.1	70.9	93.7	95
12	1.8	3.1	1.7	3.0	5.9	6.0	68	89.5	91.5
13	1.7	3.0	1.5	3.2	6.1	6.3	67.5	88.6	89
14	1.6	2.9	1.2	3.1	5.9	6.1	64.6	85.4	86.5
Mean	2.1	3.1	1.6	3.4	5.4	6.2	80.9	102.7	113

Table 4. Distribution of Cd in different fractions for the 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg/g soil)

Soil number	EX	CARB	OM	MnOX	AFeOX	CFeOX	RES	Sum	Total
1	0.89	0.29	0.136	0.165	0.25	0.156	0.3	2.18	2.25
2	0.85	0.23	0.133	0.161	0.23	0.149	0.34	2.1	2.13
3	0.832	0.216	0.13	0.156	0.22	0.146	0.2	1.9	2.0
4	0.795	0.213	0.123	0.132	0.24	0.136	0.211	1.85	1.9
5	0.765	0.205	0.116	0.118	0.218	0.145	0.133	1.7	1.8
6	0.698	0.2	0.11	0.12	0.239	0.126	0.137	1.63	1.68
7	0.66	0.018	0.09	0.11	0.234	0.116	0.232	1.46	1.5
8	0.58	0.017	0.08	0.11	0.185	0.096	0.23	1.32	1.4
9	0.58	0.014	0.076	0.095	0.176	0.091	0.268	1.30	1.45
10	0.43	0.08	0.086	0.093	0.152	0.094	0.225	1.16	1.17
11	0.389	0.085	0.078	0.086	0.093	0.091	0.163	0.985	0.99
12	0.289	0.076	0.068	0.065	0.069	0.080	0.153	0.800	0.81
13	0.263	0.066	0.063	0.059	0.061	0.064	0.209	0.785	0.79
14	0.236	0.061	0.056	0.053	0.050	0.060	0.229	0.745	0.76
Mean	0.589	0.175	0.09	0.1	0.17	0.11	0.21	1.43	1.47

From our data, an average of nearly 65-70 % of the total Cd in these soils was present in exchangeable, carbonates, and residual form (Table 5). The organic Cd fraction in these soils was significantly smaller compared to other fractions. The Cd associated with crystalline Mn and Fe oxides was very low in the soils, in contrast to the data presented from different authors, who hypothesised that these oxides are major trace metal sinks.

The residual Cd is also likely to be composed of a range of bonding tapes. This fraction may include resistant Cd oxide minerals, organically deposited on the soil from aerial sources. The distribution of Zn and Cu (Table 3 and 4) was similar to Cd, but with a reduced amount of exchangeable metal, and increased organically bound and residual fraction.

Different studies of Zn fractions (Shuman, 1979), have found up to 70% of Zn in agricultural soils in the residual fraction, and nearly all the remainder associated with Fe oxides. The high organic content and low amount of Fe and Mn appear to determine the Zn distribution found in the soils analysed in this study. Residual, organically bound, carbonate/crystalline Fe fraction were nearly equal and accounting for most of the Cu in these soils (Table 3).

Conclusions

The data presented in this study indicated that the soils around the Metallurgical plant of Elbasan are highly polluted with Cd, Zn and Cu, and that the extent of contamination is limited to the immediate industrialised region (within 20 km from the industrial centre).

A sequential extraction technique used to characterise bonding of metals to the soils showed that organic matter, carbonates and poorly crystalline Fe oxides, and tightly bound residual fractions contained > 60 % of the total Cd, Zn and Cu.

Exchangeable Cd was a significant fraction, averaging from 30 to 40 % of the total present. Although amounts of organic matter and Fe oxides were of obvious importance in influencing this distribution, there was little variation in different fractions found in this study.

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